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THERMODYNAMIC PROPERTIES OF ORGANIC DERIVATIVES OF THE LIGHTER ELEMENTS

Bartlesville Petroleum Research Center
Bureau of Mines
Bartlesville, Oklahoma

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FOREWORD

The objectives of the program are formulated within the framework of an integrated and interrelated program of experimental and theoretical research in chemical thermodynamics and thermochemistry. Emphasis is placed on areas of unclassified work that complement, wherever possible, developments in the studies of organic derivatives of the lighter elements as they relate to the thermochemical technology of possible new high energy fuels.

ABSTRACT

Measurement of the thermal properties of a mixture of ethylenimine and its dimer near the eutectic composition has provided needed information for interpreting the premelting region of pure ethylenimine. Tables of values for enthalpy of formation, Gibbs energy of formation, and logarithm of the equilibrium constant of formation of ethylenimine were calculated. Molal thermodynamic functions for the condensed phases of 1,2-diaminoethane and 1,2-diaminopropane were calculated from low-temperature calorimetric measurements.

The thermochemical properties of isobutylamine were measured in order to further define C-N bond energy in amines and diamines.

Correlations of the thermodynamic properties of hexafluorobenzene were completed from 0 to 1500°K.

I. THERMOCHEMISTRY OF ETHYLENIMINE

The high positive enthalpy of formation of ethylenimine, +30.4 kcal $mole^{-1}$, indicates considerable strain energy in the ring and in the repulsion of the ring protons. Therefore, ethylenimine derivatives that retain the ring structure are good prospects as fuel constituents. Because of the role that ethylenimine might play as an intermediate or as a reactant in fuel synthesis, the thermodynamic properties important to reaction equilibrium calculations were pursued as a basic study.

Chemical Thermodynamic Properties in the Ideal Gas State

The molal thermodynamic properties of ethylenimine in the ideal gas state from 190 to 1500°K were presented in Annual Technical Summary, March 1968, Contract No. ISSA-67-0008, Project No. 9713, Task No. 02. Values for enthalpy of formation, Gibbs energy of formation, and logarithm of the equilibrium constant of formation, Table I, complete the tables of molal thermodynamic properties. The present values are significantly different than those published by Vvedenskii[1] but the temperature trend in Gibbs energy of formation and in the equilibrium constant is similar. The trend toward more positive values of $\log_{10}Kf$ with increasing temperature is not unusual. The calculated values of the thermodynamic functions, the experimental value of the enthalpy of formation, $\Delta Hf°_{298.15}$, and the values of thermodynamic functions of C(c,graphite), H_2(g), and S_2(g)[2] were used in calculating values of $\Delta Hf°$, $\Delta Gf°$, and $\log_{10}Kf$.

Eutectic and Premelting Regions

Low-temperature calorimetric measurements on two samples of ethylenimine with different amounts of impurity (reported in Annual Technical Summary, March 1, 1967 to March 1, 1968) revealed below the melting point of ethylenimine a bump in the heat capacity curve that was assumed to be caused by the melting of a eutectic of ethylenimine and its dimer, N-(2-aminoethyl)-aziridine. When the enthalpy results in the premelting region were interpreted by ideal solution laws, approximate values of a eutectic melting point and compositions were obtained. Recent confirmatory calorimetric measurements on a prepared mixture of 76.08 mole % ethylenimine, 23.32 mole % N-(2-aminoethyl)aziridine, and the remainder unknown impurity provided enough information to accurately characterize the eutectic and confirm the previously reported values for the enthalpy and entropy of fusion of ethylenimine. Figure 1 is a schematic phase diagram of the eutectic region derived from calorimetric melting points taken at various values of fraction melted, Figure 2. The tail shown extending from the eutectic point is the

TABLE I. Molal Thermodynamic Properties of Ethylenimine in the Ideal Gas State

T, °K	$\Delta Hf°$, [a] kcal	$\Delta Gf°$, [a] kcal	$\log_{10} Kf$, [a]
0	0	0	Infinite
273.15	30.72	42.38	-33.91
298.15	30.40	43.47	-31.86
300	30.38	43.55	-31.73
400	29.24	48.12	-26.29
500	28.34	52.45	-23.14
600	27.65	57.94	-21.10
700	27.14	63.04	-19.68
800	26.77	68.19	-18.63
900	26.51	73.37	-17.82
1000	26.37	78.59	-17.18
1100	26.31	83.82	-16.65
1200	26.32	89.05	-16.22
1300	26.38	94.27	-15.85
1400	26.50	99.50	-15.53
1500	26.64	104.70	-15.25

[a] For the reaction

$$2\,C(c,\text{graphite}) + 5/2\,H_2(g) + 1/2\,N_2(g) = C_2H_5N(g)$$

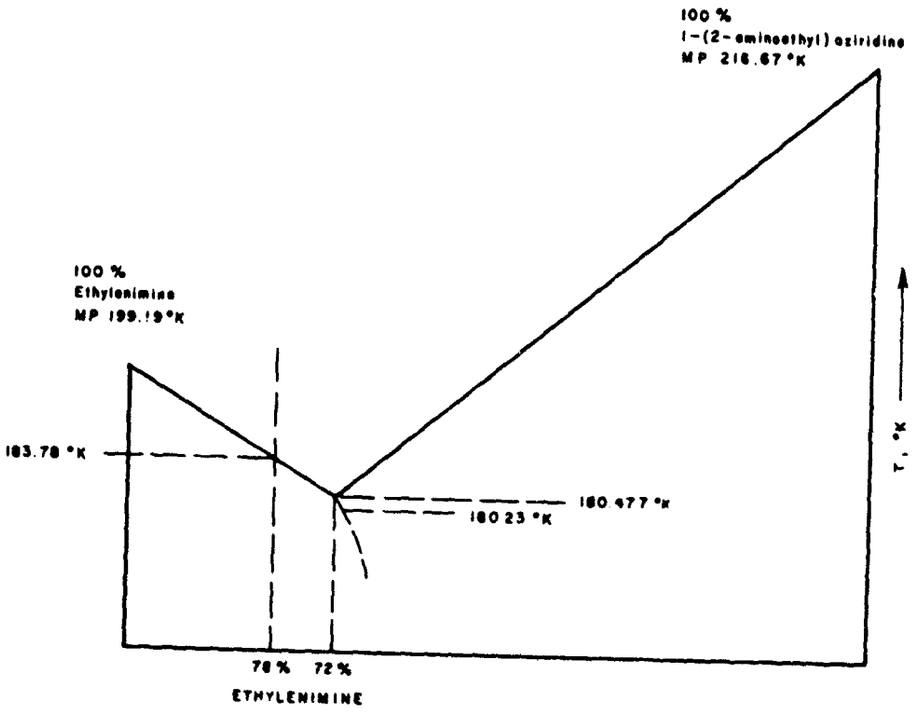


FIGURE 1.- Ethylenimine - Dimer Phase Diagram (Schematic).

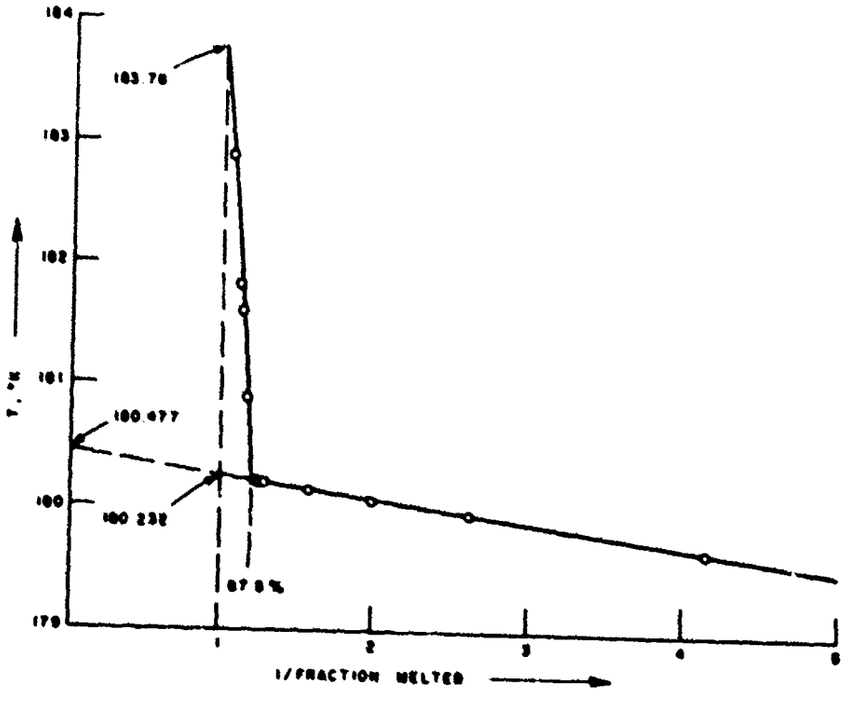


FIGURE 2.- Melting Behaviour of Mixture .

schematic trace of a lowering of the eutectic point by a third material present as an impurity in the binary system. The derived value for the heat of fusion of the eutectic is 1611 cal $mole^{-1}$, and the estimated value for the heat of fusion of the dimer at its assumed melting point of 216.67°K is 3180 cal $mole^{-1}$.

II. THERMOCHEMISTRY OF ALIPHATIC DIAMINES

A better understanding of the possible variation of the N-F thermochemical bond energy, and of the thermochemical properties of the NF_2 compounds, with molecular structure can be derived through a more complete knowledge of these quantities for related diamines. In the Annual Technical Summary Report, March 1, 1966 to March 1, 1967, and Annual Technical Summary Report, March 1, 1967 to March 1, 1968, enthalpies of combustion and formation were reported for 1,2-diaminopropane, 1,2-diaminoethane, 1,2-diamino-2-methylpropane, 1,2-diaminobutane, and 1,2-diamino-2-methylpropane; low-temperature calorimetric measurements were reported for 1,2-diaminoethane and 1,2-diaminopropane; vapor pressures were reported for 1,2-diaminobutane, 1,2-diamino-2-methylpropane,and the solid and liquid phases of 1,2-diaminoethane; and enthalpies of vaporization calculated for 1,2-diaminoethane, 1,2-diaminobutane, 1,2-diamino-2-methylpropane, and 1,2-diaminopropane.

Calculated values for the thermodynamic functions of the condensed phases of 1,2-diaminopropane and 1,2-diaminoethane, Table II, were obtained from low-temperature calorimetric measurements previously reported for these compounds.

Low-temperature calorimetric measurements were completed for 1,2-diamino-2-methylpropane and calculation of its thermodynamic properties are in progress. Measurements were complicated by impurities in the sample that led to irregularities in the heat capacity in the premelting region. The sample of 1,2-diamino-2-methylpropane melted at 254.66°K. From the slope of a preliminary plot of the temperature vs. reciprocal of the fraction melted, a value of 256.6°K was estimated for the triple point of the pure material. The sample purity, 99.2 mole %, was calculated from the simplified relation of the melting point depression, $N_2^* = AF\Delta T$, where N_2^* is the mole fraction of impurity, F is the fraction of the sample melted, ΔT is the difference between the triple point temperature and the equilibrium temperature at F, and A is the cryoscopic constant, $\Delta Hm/RT^2_{TP} = 0.00428\ deg^{-1}$. The small values of the heat of fusion, 561 cal $mole^{-1}$, and entropy of fusion, 2.19 cal deg^{-1} $mole^{-1}$, are typical of globular molecules. A large solid-solid transition was found near 237.5°K where the main energy absorption occurred. A large upsweep before (and a downsweep after) the transition was noted in the heat

TABLE II. Molal Thermodynamic Functions for Condensed Phases
(Preliminary)

T, °K	$-(G_s-H^\circ_0)/T$, cal deg^{-1}	$(H_s-H^\circ_0)/T$, cal deg^{-1}	$H_s-H^\circ_0$, cal	S_s, cal deg^{-1}	C_s, cal deg^{-1}
		1,2-Diaminopropane			
		Crystals			
10	0.017	0.051	0.51	0.068	0.203
12	0.029	0.088	1.05	0.117	0.350
14	0.047	0.139	1.94	0.185	0.547
16	0.069	0.205	3.28	0.274	0.798
18	0.098	0.287	5.16	0.385	1.087
20	0.133	0.382	7.64	0.515	1.405
25	0.249	0.676	16.88	0.924	2.312
30	0.402	1.028	30.85	1.431	3.280
35	0.590	1.421	49.74	2.011	4.268
40	0.806	1.835	73.40	2.641	5.188
45	1.047	2.258	101.60	3.305	6.093
50	1.307	2.686	134.27	3.992	6.964
60	1.872	3.531	211.84	5.402	8.527
70	2.478	4.348	304.35	6.826	9.938
80	3.110	5.128	410.2	8.238	11.249
90	3.757	5.880	529.1	9.637	12.510
100	4.414	6.609	659.9	11.013	13.621
110	5.076	7.289	801.7	12.364	14.737
120	5.739	7.953	954.3	13.692	15.795
130	6.401	8.597	1117.6	14.998	16.845
140	7.061	9.222	1291.0	16.283	17.834
150	7.718	9.829	1474.2	17.547	18.810
160	8.371	10.420	1667.2	18.791	19.780
170	9.020	10.997	1869.5	20.018	20.666
180	9.665	11.559	2080.6	21.224	21.554
190	10.305	12.109	2300.6	22.413	22.444
200	10.939	12.647	2529.3	23.586	23.284
210	11.569	13.173	2766.3	24.742	24.232
220	12.195	13.740	3022.8	25.935	27.680
230	12.816	14.234	3273.8	27.050	26.676
236.52	13.219	14.595	3452.0	27.814	28.016
		Liquid			
236.52	13.22	33.16	7842	46.38	47.98
240	13.70	33.37	8009	47.07	48.04
250	15.08	33.96	8491	49.04	48.23
260	16.42	34.51	8974	50.93	48.40

TABLE II. Molal Thermodynamic Functions for Condensed Phases--Continued
(Preliminary)

T, °K	$-(G_s-H^\circ_0)/T$, cal deg^{-1}	$(H_s-H^\circ_0)/T$, cal deg^{-1}	$H_s-H^\circ_0$, cal	S_s, cal deg^{-1}	C_s, cal deg^{-1}
		1,2-Diaminopropane			
		Liquid			
270	17.73	35.03	9459	52.76	48.56
273.15	18.14	35.19	9612	53.33	48.61
280	19.01	35.52	9945	54.53	48.72
290	20.27	35.98	10434	56.25	48.97
298.15	21.27	36.34	10833	57.61	49.15
300	21.50	36.41	10924	57.91	49.18
310	22.70	36.83	11417	59.53	49.38
320	23.87	37.23	11912	61.10	49.63
330	25.02	37.61	12410	62.63	49.91
340	26.15	37.97	12911	64.12	50.22
350	27.26	38.33	13415	65.59	50.55
360	28.34	38.67	13922	67.01	50.87
370	29.41	39.00	14433	68.41	51.29
380	30.45	39.34	14948	69.79	51.84
		1,2-Diaminoethane			
		Crystals			
10	0.008	0.023	0.23	0.031	0.095
12	0.014	0.041	0.49	0.055	0.169
14	0.022	0.067	0.94	0.088	0.279
16	0.033	0.102	1.63	0.135	0.426
18	0.047	0.148	2.67	0.195	0.613
20	0.066	0.205	4.10	0.271	0.829
25	0.131	0.394	9.84	0.524	1.491
30	0.223	0.640	19.21	0.864	2.270
35	0.344	0.932	32.64	1.276	3.103
40	0.489	1.256	50.23	1.745	3.934
45	0.656	1.599	71.96	2.256	4.754
50	0.843	1.955	97.76	2.799	5.565
60	1.264	2.682	160.93	3.946	7.048
70	1.732	3.402	238.12	5.133	8.352
80	2.231	4.093	327.42	6.324	9.512
90	2.752	4.755	427.9	7.507	10.574
100	3.286	5.384	538.4	8.670	11.508
110	3.827	5.981	657.8	9.808	12.379
120	4.372	6.549	785.9	10.921	13.218
130	4.918	7.093	922.1	12.011	14.024

TABLE II. Molal Thermodynamic Functions for Condensed Phases--Continued
(Preliminary)

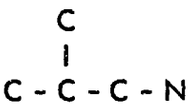
T, °K	$-(G_s-H^\circ_0)/T$, cal deg^{-1}	$(H_s-H^\circ_0)/T$, cal deg^{-1}	$H_s-H^\circ_0$, cal	S_s, cal deg^{-1}	C_s, cal deg^{-1}
		1,2-Diaminoethane			
		Crystals			
140	5.463	7.616	1066.2	13.079	14.805
150	6.006	8.121	1218.0	14.126	15.544
160	6.545	8.607	1377.1	15.153	16.275
170	7.082	9.080	1543.6	16.162	17.022
180	7.614	9.546	1718.2	17.159	17.826
190	8.145	10.222	1942.2	18.367	28.490
200	8.687	10.880	2176.0	19.567	21.927
210	9.230	11.377	2389.2	20.608	20.899
220	9.770	11.806	2597.2	21.575	20.841
230	10.303	12.208	2807.7	22.511	21.310
240	10.831	12.599	3023.7	23.430	21.981
250	11.354	12.989	3247	24.343	22.743
260	11.871	13.379	3478	25.250	23.496
270	12.383	13.768	3717	26.151	24.285
280	12.891	14.158	3964	27.048	25.060
284.29	13.107	14.325	4072	27.432	25.392
		Liquid			
284.29	13.11	33.31	9469	46.42	41.04
290	13.77	33.46	9704	47.23	41.13
298.15	14.70	33.67	10040	48.37	41.25
300	14.91	33.72	10116	48.63	41.28
310	16.02	33.96	10530	49.98	41.46
320	17.10	34.20	10945	51.30	41.65
330	18.16	34.43	11363	52.59	41.87
340	19.18	34.66	11783	53.84	42.12

capacity curve. Part of this can be explained and corrected for by assuming that the increase in the heat capacity of the sample under study is the result of "premelting." In the temperature region 202 to 218°K a small "bump" in the heat capacity curve was noted. This "bump" could be partially supercooled and was reproducible only by slow, careful cooling which yielded equilibrium conditions. This anomaly in the heat capacity curve can be explained by eutectic melting.

III. THERMOCHEMISTRY OF ISOBUTYLAMINE

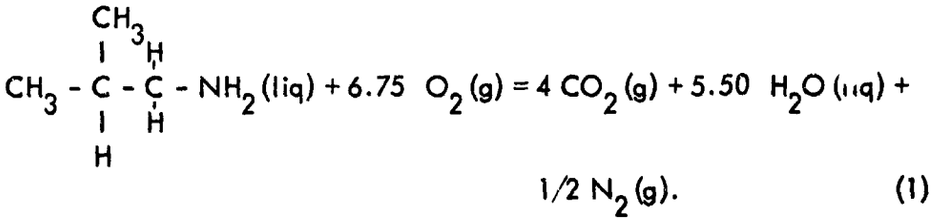
Enthalpy of Combustion and Formation

A value of the C-N thermochemical bond energy in the molecular configuration (I)



(I)

was needed to interpret results for the C-N bond energy in the diamines. The value of $\Delta Ec°/M$, the energy of the idealized combustion reaction, for isobutylamine was found to be -9829.50 ± 0.21 cal g^{-1} (mean and standard deviation for eight experiments). This value of $\Delta Ec°/M$ refers to the reaction (1)



$$1/2\ N_2\,(g). \qquad (1)$$

The value of the standard enthalpy of combustion according to reaction 1, $\Delta Hc°_{298.15}$, is -720.25 ± 0.10 kcal $mole^{-1}$ (mean value with uncertainty interval). This value was combined with currently accepted values of the enthalpies of formation of gaseous CO_2 and liquid H_2O to obtain the enthalpy of formation of liquid isobutylamine (equation 2).

$$4\ C(c,\text{graphite}) + 11/2\ H_2\,(g) + 1/2\ N_2\,(g) = C_4H_{11}N\,(liq) \qquad (2)$$

$$\Delta Hf°_{298.15} = -31.68 \pm 0.12 \text{ kcal mole}^{-1}\ .$$

The enthalpy of vaporization of isobutylamine (derived from vapor pressure measurements also reported) was combined with the enthalpy of formation of the liquid in order to estimate the enthalpy of formation of the ideal gas (equation 3).

$$4\,C(c,\text{graphite}) + 11/2\,H_2(g) + 1/2\,N_2(g) = C_4H_{11}N(g) \qquad (3)$$

$$\Delta Hf^\circ_{298.15} = -23.57 \pm 0.13 \text{ kcal mole}^{-1}.$$

The value of E(C-N), the carbon-nitrogen thermochemical bond energy, in isobutylamine was found to be 69.0 kcal.

Vapor Pressure and Enthalpy of Vaporization

Results of measurements by the ebulliometric method, Table III, were correlated with the Cox vapor pressure equations. Appropriate weighting in the least-squares program was employed. Enthalpies of vaporization were obtained at 25°C from the Clapeyron equation with the dP/dT's from the Cox equation.

IV. THERMOCHEMISTRY OF BORAZOLE, $B_3N_3H_6$

The instability of borazole has prevented purification of a large enough sample for a comprehensive calorimetric study. A 3-ml sample was finally obtained by gas-liquid chromatography for measurement of its vapor pressure by the inclined-piston method at low temperatures. However, the sample slowly decomposed in the vapor phase of the piston chamber. Possible modification of the method to remove the direct contact of borazole vapor from the piston is being reviewed. Until successful vapor pressure determinations are made, other phases of work on borazole will be postponed.

V. STATE AND THERMODYNAMIC PROPERTIES OF FLUORINE COMPOUNDS

Previously, in the Annual Technical Summary Reports for March 1, 1966 to March 1, 1967 and March 1, 1967 to March 1, 1968, results of vapor heat capacity and P-V-T studies of hexafluorobenzene were reported.

Intermolecular Potential Energy of Hexafluorobenzene

Parameters have been determined for the Stockmayer potential energy function which represents the second virial coefficients determined from both the high-

TABLE III. Vapor Pressure of Isobutylamine
Ebulliometric Method

t, °C	p(obsd), mmHg	p(obsd), mm - p(calcd), mm Hg*
16.037	92.52	-0.02
18.512	104.63	0.00
20.995	118.06	+0.02
23.494	132.95	+0.02
26.006	149.41	0.00
31.053	187.57	-0.02
36.141	233.72	-0.02
41.269	289.13	+0.01
46.443	355.22	+0.01
51.660	433.56	+0.01
56.921	525.86	0.00
62.226	633.99	0.00
67.576	760.00	0.00
72.970	906.06	+0.01
78.410	1074.60	+0.05
83.894	1268.00	+0.02
89.425	1489.10	-0.06
94.998	1740.80	+0.02
100.615	2026.00	0.00

*Cox equation: $\log_{10}(p/760) = A(1 - 340.726/T)$,

where $\log_{10}A = +0.9213782 - 1.044289 \times 10^{-3}T + 1.086212 \times 10^{-6}T^2$

$\Delta Hv_{298.15°K} = 8110$ calories

temperature P-V-T data and also from the low-temperature heat-of-vaporization and vapor-pressure data. Thus, an excellent thermodynamic consistency check was established between the P-V-T and vapor heat capacity data. In addition, hexafluorobenzene was shown to be a hard molecule, relative to fluorobenzene, and to have an unsymmetrical potential energy field which can be represented, empirically, by the Stockmayer potential which has an orientational term.

Vapor Heat Capacity of Hexafluorobenzene

Heats of vaporization of hexafluorobenzene appeared in Annual Technical Summary Report, March 1, 1965 to March 1, 1966. Final values of calorimetrically determined heat capacities at constant pressure are in Table IV.

TABLE IV. Molal Heat Capacity, C_p, of Hexafluorobenzene Gas in Calories per Degree

P, atm	Temperature, °C							
	62	75	90	130	165	200	227	254
2				45.560	46.807	48.256	49.332	50.341
1			43.093	44.643	46.268	47.874	49.024	50.116
1/2		41.415	42.431	44.240	46.006	47.676	48.895	50.002
3/8	40.532	41.185	42.274					
1/4	40.274	40.991	42.148	44.077	45.921	47.640	48.903	49.989
3/16	40.124							
1/8	40.006	40.774						
0	39.752	40.577	41.847	43.872	45.790	47.532	48.802	49.921
$\left(\frac{\partial C_p}{\partial P}\right)_T^*$ $P \to 0$	1.986	1.576	1.127	0.736	0.456	0.333	0.240	0.196

* cal/deg-mol-atm

Chemical Thermodynamic Properties of Hexafluorobenzene

Thermodynamic functions (Gibbs energy function, enthalpy function, enthalpy, entropy, and heat capacity) were calculated for hexafluorobenzene in the ideal gas state. Two unobserved vibrational wavenumbers and two constants of an empirical anharmonicity function, four quantities in all, were selected to give agreement with calorimetric values of entropy and heat capacity. The thermodynamic functions were used with a calorimetric value of the standard enthalpy of formation and other pertinent data to calculate values of the standard enthalpy of formation, the standard Gibbs energy of formation, and the common logarithm of the equilibrium constant of formation for selected temperatures between 0 and 1500°K, Tables V and VI.

TABLE V. Observed and Calculated Entropy and Heat Capacity of Hexafluorobenzene

Entropy, S°, cal deg^{-1} $mole^{-1}$			Heat Capacity, C_p°, cal deg^{-1} $mole^{-1}$		
T, °K	Obs	Calc	T, °K	Obs	Calc
300.58	91.76	91.74	335.15	39.75	39.73
315.96	93.65	93.63	348.15	40.58	40.58
333.41	95.72	95.73	368.15	41.85	41.84
353.40	98.05	98.07	403.15	43.87	43.90
376.52	100.66	100.71	438.15	45.79	45.80
			473.15	47.53	47.53
			500.15	48.80	48.77
			527.15	49.92	49.93

TABLE VI. Molal Thermodynamic Properties of Hexafluorobenzene in the Ideal Gas State [a]

T, °K	$(G^\circ - H^\circ_0)/T$, cal deg^{-1}	$(H^\circ - H^\circ_0)/T$, cal deg^{-1}	$H^\circ - H^\circ_0$, kcal	S°, cal deg^{-1}	C_p°, cal deg^{-1}	ΔHf°, [b] kcal	ΔGf°, [b] kcal	$\log_{10} Kf$ [b]
0	0	0	0	0	0	-223.16	-223.16	∞
273.15	-67.17	21.10	5.762	88.27	35.28	-224.38	-207.38	165.92
298.15	-69.07	22.37	6.668	91.44	37.16	-224.33	-205.83	150.87
300	-69.21	22.46	6.737	91.67	37.30	-224.33	-205.71	149.86
400	-76.31	27.00	10.80	103.31	43.72	-224.05	-199.55	109.03
500	-82.77	30.87	15.44	113.64	48.77	-223.75	-193.46	84.56
600	-88.70	34.19	20.52	122.89	52.67	-223.43	-187.43	68.27
700	-94.18	37.06	25.94	131.24	55.67	-223.11	-181.45	56.65
800	-99.30	39.53	31.63	138.83	57.98	-222.78	-175.53	47.95
900	-104.08	41.69	37.52	145.77	59.78	-222.44	-169.64	41.19
1000	-108.58	43.57	43.57	152.15	61.20	-222.07	-163.80	35.80
1100	-112.81	45.23	49.75	158.04	62.34	-221.71	-157.98	31.39
1200	-116.81	46.69	56.03	163.50	63.27	-221.34	-152.21	27.72
1300	-120.60	48.00	62.40	168.60	64.03	-220.97	-146.46	24.62
1400	-124.20	49.17	68.84	173.37	64.67	-220.59	-140.74	21.97
1500	-127.63	50.22	75.33	177.85	65.21	-220.21	-135.06	19.68

[a] To retain internal consistency, some values are given to one more decimal place than is justified by the absolute accuracy.

[b] The standard enthalpy, Gibbs energy, and common logarithm of the equilibrium constant of formation by the reaction, $6C(c,graphite) + 3\ F_2(g) = C_6F_6(g)$.

VI. PURIFICATION OF SAMPLES

Purification of samples of cyclopropylamine and N-(2-aminoethyl)aziridine are in progress on a GLC Megachrom unit. About 17 ml of cyclopropylamine were prepared for heats-of-combustion measurements. In addition, 65 ml will be prepared for vapor pressure and low-temperature calorimetric measurements.

VII. PUBLICATIONS

"Thermochemistry of Ethylenimine and Some Diamines" by W. D. Good, H. L. Finke, J. F. Messerly, G. B. Guthrie, R. H. Harrison, and D. R. Douslin, Proceedings of the Thermochemistry Working Group Symposium, Douglas Advanced Research Laboratory, Huntington Beach, Calif., March 25-27, 1968. CPIA Pub. 173

"Pressure-Volume-Temperature Relations of Hexafluorobenzene" by D. R. Douslin, R. H. Harrison, and R. T. Moore. (In press)

"The Enthalpies of Combustion and Formation of 1,1'-Bis(difluoroamino)heptane. The N-F Thermochemical Bond Energy" by W. D. Good and N. K. Smith. (In press)

"The Enthalpies of Formation of Ethylenediamine, 1,2-Propanediamine, 1,2-Butanediamine, 2-Methyl-1,2-propanediamine, and Isobutylamine. The C-N and N-F Thermochemical Bond Energies" by W. D. Good and R. T. Moore. (In press)

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13. ABSTRACT

Measurement of the thermal properties of a mixture of ethylenimine and its dimer near the eutectic composition has provided needed information for interpreting the premelting region of pure ethylenimine. Tables of values for enthalpy of formation, Gibbs energy of formation, and logarithm of the equilibrium constant of formation of ethylenimine were calculated. Molal thermodynamic functions for the condensed phases of 1,2-diaminoethane and 1,2-diaminopropane were calculated from low-temperature calorimetric measurements.

The thermochemical properties of isobutylamine were measured in order to further define C-N bond energy in amines and diamines.

Correlations of the thermodynamic properties of hexafluorobenzene were completed from 0 to 1500°K.

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14. KEY WORDS		LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Thermochemistry	Ethylenimine						
Enthalpy of formation	1,2-Diaminoethane						
Entropy of formation	1,2-Diaminopropane						
Gibbs energy of formation	1,2-Diamino-2-methylpropane						
Bond energies							
Vapor pressure	Isobutylamine						
Enthalpy of vaporization	Hexafluorobenzene						
Thermal properties	Borazole						
State properties							
Vapor Heat Capacity							

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